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(71)Applicant : NIPPON POLYCHEM KK

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## (54) LAMINATE, RESIN OR RESIN COMPOSITION FOR FORMING LAMINATE AND METHOD FOR TREATING THE LAMINATE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a packing laminate advantageous in economy by improving a working environment with satisfactory heat sealability and low odor, securing safety and reducing number of steps.

SOLUTION: The laminate comprises a base material layer which is not anchor-coated and ethylene- $\alpha$ -olefin copolymer resin in such a manner that adhesive strength of the laminate is 300 g/15 mm width or more. In the laminate forming resin composition for forming the laminate by extrusion laminating at least one side surface of the layer, the laminate forming resin or resin composition has MFR of 1 to 100 g/10 min, a density of 0.900 g/cm or lower and relationship between an extrapolation melting finishing temperature(Tem) of a melting peak and the density satisfying a relational formula of  $tem \leq 286D - 137$ . And the laminate is

heat treated at 40°C or higher.

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## MEANS

[Means for Solving the Problem] As a result of repeating research wholeheartedly in view of the above-mentioned trouble, even if this invention person low-temperature-izes the extrusion temperature of thermoplastics by using the resin of a character [ \*\*\*\* ], he used to come to complete this invention based on knowledge that the layered product from which anchor-coat processing was not performed but which \*\* also excelled in the bond strength of a base-material layer and a glue line is obtained. That is, the layered product of this invention is a layered product which consists of a resin constituent layer containing the base-material layer, the ethylene and the alpha olefin copolymer resin, or this copolymer resin to which anchor-coat processing is not performed, and is characterized by the bond strength of this layered product being more than 300g/15mm width of face. Moreover, the resin for layered product formation or resin constituent which is another invention of this invention In the resin for layered product formation or resin constituent for carrying out an extrusion lamination and forming a layered product at least in one side of a base-material layer to which anchor-coat processing is not performed This resin for layered product formation or a resin constituent is 1-100g of MFRs, and 10 minutes, and it is density 0.900 g/cm<sup>3</sup>. Relation between the extrapolation dissolution end temperature (Tem) of a dissolution peak and density is hereafter characterized by being what fills the following relational expression.

$$Tem \leq 286D - 137$$
-- after the art of the layered product which is another invention of this invention carries out the extrusion lamination of the resin constituent which contains ethylene and the alpha olefin copolymer resin, or this copolymer resin at least on one side of the base-

material film with which anchor-coat processing is not performed and considers as a layered product, it is characterized by heat-treating this layered product at the temperature of 40 degrees C or more again

[0006]

[Embodiments of the Invention]

[I] Layered product (1) The bond strength of the base-material layer and glue line to which the layered product of a lamination this invention carries out the laminating of the glue line which turns into a base-material layer to which anchor-coat processing is not performed from ethylene and the alpha olefin copolymer resin, and the aforementioned anchor-coat processing is not performed is the thing of 300 - 500g/15mm width of face preferably more than 300g/15mm width of face.

[0007] (i) As a material used for the base-material layer of the layered product of a base-material layer this invention, metallic foils, such as un-extending or the oriented film of synthetic resin, such as polyamide resin, such as polyester resin, such as polyolefin resin, a saponification object of an ethylene vinylacetate copolymer, polystyrene resin, and a polyethylene terephthalate (PET), and nylon, a polyvinyl alcohol resin, a polyvinyl chloride resin, and a polyvinylidene chloride resin, a sheet or aluminum, iron, and copper, or a metal plate, textile fabrics or a nonwoven fabric, paper, cellophane, etc. can be mentioned It is desirable to use polyamide resin, such as polyester, such as a polyethylene terephthalate (PET), and a nylon oriented film (ONY), a polypropylene oriented film (OPP), and a metallic foil also in these. Generally as for the above-mentioned base-material layer, 7-200 micrometers of things with a thickness of 7-50 micrometers are used preferably. These can also perform a corona treatment, frame processing, ozonization, etc. for the front face if needed.

[0008] (ii) It is the resin constituent which contains the copolymer resin obtained from ethylene and an alpha olefin (alpha olefin which is the molecule skeleton of 3-10 carbon numbers especially preferably 3-18 carbon numbers preferably), or this copolymer resin as the ethylene and alpha olefin copolymer resin used as a glue line of the layered product of a glue-line this invention. It is the resin constituent which specifically contains the copolymer resin obtained from one sort of the alpha olefin of ethylene, butene-1 and a hexene -1, an octene -1, and 4-methyl pentene-1 grade, or two sorts or more of mixture, or this copolymer resin. Generally as for the above-mentioned glue line, 10-100 micrometers of things with a thickness of 15-50 micrometers are used preferably.

[0009] (iii) Other layers (arbitrary layer)

An arbitrary layer can be formed in addition to the base-material layer in the layered product of this invention, and the indispensable layer of a glue line. As a material used for this arbitrary layer, polyolefine system resins, such as polyethylene system resins, such as a high-pressure-produced-polyethylene resin and an ethylene-vinylacetate-copolymer resin, and a polypropylene resin, etc. can be mentioned. Generally as for the above-mentioned arbitrary layer, 1-100 micrometers of things with a thickness of 10-50 micrometers are used preferably.

[0010] [II] Ethylene and alpha olefin copolymer resin constituent (1) Ethylene and alpha olefin copolymer resin (component A)

(a) Object As for the sex above-mentioned ethylene and an alpha olefin copolymer resin, it is desirable to use what shows the following physical properties.

\*\* 1-100g / thing that shows 3-50g / 10 minutes preferably is used for MFR (melt flow rate : melting flow rate) according [ the ethylene and the alpha olefin copolymer resin used in an MFR this invention ] to JIS-K7210 for 10 minutes. Adhesion with a base-material layer will become it small that this MFR is under the above-mentioned range, and the spread nature of a resin will be lost. Moreover, if this MFR exceeds the above-mentioned range, the neck in will be large and a melting thin film with the uniform case of a gap will not be obtained.

[0011] \*\* Dense For the ethylene and the alpha olefin copolymer resin used in a degree this

invention, the density (D) by JIS-K7112 is 0.900 g/cm<sup>3</sup>. They are 0.895 g/cm<sup>3</sup> preferably hereafter. It is 0.890 - 0.865 g/cm<sup>3</sup> especially preferably hereafter. What is shown is used. If this density is larger than the above-mentioned range, an adhesive property with a base-material layer will become small, and a layered product with strong intensity will not be obtained.

[0012] \*\* Extrapolation dissolution end temperature of the dissolution peak by the differential scanning calorimetry (DSC) (Tem)

The line which extended the base line by the side of the elevated temperature of the DSC curve by which the ethylene and the alpha olefin copolymer resin used in this invention were measured based on JIS-7121 to the low temperature side, The relation of the extrapolation dissolution end temperature (Tem) and density (D) which are the temperature of an intersection with the tangent drawn in that the inclination of the curve by the side of the elevated temperature of a dissolution peak serves as the maximum  $Tem \leq 286D - 137$  -- they are  $Tem \leq 349D - 197$  and the thing which satisfies the relational expression of  $Tem \leq 429D - 271$  most preferably preferably

[0013] (b) manufacture of ethylene and the alpha olefin copolymer resin -- although such ethylene and alpha olefin copolymer resin may be the thing manufactured using the metallocene system catalyst shown below and the thing manufactured using the conventional vanadium system catalyst, and \*\*\*\*\*, what was manufactured using the metallocene catalyst is desirable

[0014] As a resin manufactured using the resin metallocene catalyst manufactured using the metallocene catalyst JP,58-19309,A, JP,59-95292,A, JP,60-35005,A, JP,60-35006,A, JP,60-35007,A, JP,60-35008,A, Each official report of JP,60-35009,A, JP,61-130314,A, and JP,3-163088,A, The European Patent application public presentation No. 420,436 specification, a U.S. Pat. No. 5,055,438 specification, And the method indicated by the international public presentation official report WO 91/No. 04257 specification etc., i.e., a metallocene catalyst, a metallocene/alumoxane catalyst, Or the catalyst which consists of a compound which reacts with a metallocene compound and a metallocene catalyst which are indicated by the international public presentation official report WO 92/No. 07123 specification etc., for example, and serves as stable ion is used. Copolymerization of the ethylene of a principal component and the alpha olefin of an accessory constituent is carried out, and they are manufactured.

[0015] As a resin manufactured using the resin vanadium system catalyst manufactured using the vanadium system catalyst, depending on the method indicated by JP,52-39741,A, i.e., a vanadium compound and an organoaluminium compound, and the case, further, the catalyst which comes to add a third component is used and it is manufactured by copolymerizing the ethylene of a principal component, and the alpha olefin of an accessory constituent.

[0016] (2) Combination resinous principle (component B)

Although the above-mentioned ethylene and alpha olefin copolymer resin (component A) can also be used independently, it is desirable to use the ethylene and the alpha olefin copolymer resin content constituent which blended with this ethylene and alpha olefin copolymer resin combination resinous principles (component B), such as a resin which can raise the low-density-polyethylene resin for an extrusion lamination and/or extrusion lamination aptitude. It is desirable to use the low-density-polyethylene resin for an extrusion lamination also in these.

[0017] (i) What shows the following physical properties as a low-density-polyethylene resin for the low-density-polyethylene resin above-mentioned extrusion lamination for an extrusion lamination is suitable.

\*\* As a low-density-polyethylene resin used in the ethylene and the alpha olefin copolymer resin constituent of an MFR this invention, 1-50g / thing that shows the physical properties for 3-20g / 10 minutes preferably is used for MFR (melt flow rate : melting flow rate) by JIS-

K7210 for 10 minutes. If the spread nature of a resin is lost as this MFR is under the above-mentioned range, and this MFR exceeds the above-mentioned range, the neck in will be large and a melting thin film with the uniform case of a gap will not be obtained.

[0018] \*\* dense the density according to JIS-K7112 as a low-density-polyethylene resin used in the ethylene and the alpha olefin copolymer-resin constituent of a degree this invention -- 0.915 - 0.930 g/cm<sup>3</sup> -- desirable -- 0.918-0.925g/cm<sup>3</sup> What is shown is used. If this density is larger than the above-mentioned range, an adhesive property with a base material will become small, and a layered product with strong intensity will not be obtained.

[0019] (3) As the ethylene and alpha olefin copolymer resin (component A) contained in the blending-ratio-of-coal above-mentioned ethylene and an alpha olefin copolymer-resin constituent, it is especially used preferably 30 to 100% of the weight at least 20% of the weight by 40 - 80% of the weight of the blending ratio of coal. The combination resinous principle (component B) added in ethylene and an alpha olefin copolymer-resin constituent is especially used preferably ten to 70% of the weight 80 or less % of the weight by 20 - 60% of the weight of the blending ratio of coal. If there are not much too many loadings of the combination resinous principle (component B) added in the above-mentioned ethylene and alpha olefin copolymer-resin constituent, an adhesive property with a base-material layer will become small conversely. On the other hand, when there were too few loadings of the combination resinous principle (component B) added in ethylene and an alpha olefin copolymer-resin constituent and extrusion lamination is carried out by the monolayer, a neck in becomes large, and a uniform melting thin film is not obtained.

[0020] (4) Other combination components (arbitrary component)

Inorganic bulking agents, such as additives, such as a slipping agent, an antistatic agent, an antifogger, an ultraviolet ray absorbent, and an antioxidant, and a calcium carbonate, a silica, titanium oxide, talc, a pigment, etc. can be added to the grade which does not bar an adhesive property with a base-material layer to the resin constituent which blended the combination resinous principle (component B) with the above-mentioned ethylene and alpha olefin copolymer resin (component A), or this copolymer resin (component A).

[0021] [III] Manufacture of a layered product (1) As a method of manufacturing the layered product of the laminating method this invention, although various methods are employable, it is desirable to adopt the method of \*\* - \*\* shown below.

\*\* Carry out the extrusion lamination of ethylene and the alpha olefin copolymer resin on the base-material film with which it is not given to anchor-coat processing, and obtain a layered product.

\*\* On the base-material film with which it is not given to anchor-coat processing, carry out an extrusion lamination, carry out the laminating of ethylene and the alpha olefin copolymer resin, subsequently to an ethylene and alpha olefin copolymer-resin layer top, carry out the extrusion lamination of other resins, and obtain a layered product.

\*\* Carry out the sandwiches extrusion lamination of ethylene and the alpha olefin copolymer resin between the base-material layer which is not given to anchor-coat processing and other resin film layers, and obtain a layered product.

\*\* On the base-material film with which ethylene and the alpha olefin copolymer resin, and the good resin of extrusion lamination fitness are not given to anchor-coat processing, carry out a co-extrusion lamination in the state of the laminating which made the aforementioned ethylene and alpha olefin copolymer resin the base-material side, and obtain a layered product.

In addition, in order to carry out the extrusion lamination of ethylene and the alpha olefin copolymer resin by the monolayer in the above-mentioned \*\* - \*\* and to raise the extrusion lamination fitness of the aforementioned ethylene and alpha olefin copolymer resin, it is desirable to consider as the ethylene and the alpha olefin copolymer-resin constituent which added the low-density-polyethylene resin for an extrusion lamination or the resin which can,

in addition to this, raise the above-mentioned extrusion lamination fitness.

[0022] (2) Laminating conditions (i) Generally as resin temperature at the time of carrying out an extrusion lamination and carrying out the laminating of laminating temperature ethylene and the alpha olefin copolymer resin, 150-320 degrees C is preferably performed at 200-300 degrees C. This resin temperature becomes poor [ the spread nature of a resin ] under at the above-mentioned temperature requirement, and a melting film becomes inadequate [ a bond strength with about / not being obtained smoothly / and a base-material layer ]. On the other hand, if resin temperature exceeds the above-mentioned temperature requirement, while problems, such as a fall of the heat-sealing nature as a laminated material and generating of an odor, will arise, a gel object is generated and problems, such as a fall of a mechanical strength and appearance, occur. In addition, it is important for a base-material layer to carry out a sticking-by-pressure lamination, using [ 190-320 degrees C is 200-300 degrees C still more preferably preferably, and extrude ethylene and the alpha olefin copolymer resin, and ] a processing side as an adhesion side subsequently, from an adhesive property with a base-material layer, and a viewpoint of an odor, after ozonizing a melting film, a melting film, nothing, and.

[0023] (ii) Meat When forming ethylene and the alpha olefin copolymer resin by the monolayer and fabricating the thickness of the coat layer at the time of carrying out a thick extrusion lamination by 10-40 micrometers and co-extrusion generally, it is a 3-35-micrometer melting film. As for air GIAPPU of a laminator, it is common to usually be carried out by 100-150mm. Moreover, about lamination speed, it is desirable to be carried out by part for 80-150m/generally from a viewpoint of productivity.

[0024] [IV] The layered product of the heat treatment this invention of a layered product can strengthen a bond strength further by heat-treating 40 degrees C or more, after carrying out the laminating of film-like a base-material layer and a glue line. The processing under the atmosphere in which this heat treatment was contacted to the heated roll, the inside of oven was passed, or \*\* was heated is adopted. Less than 40 degrees C of a treatment effect of the temperature of this heat treatment are not enough, and a bond strength does not improve. This heat treatment is performed by being usually 100-150m speed for /about the inside of the heat-treatment process in the inside of the contact or the oven to a roll, and generally, usually processing a layered product for 2 - 3 seconds.

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## EXAMPLE

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[Example] this invention does not have the range restrained by the following examples and examples of comparison, although an example and the example of comparison are indicated below and this invention is explained to it still more concretely, unless the summary is exceeded.

[I] The measurement of physical properties and the evaluation of film physical properties in the evaluation method example and the example of comparison were carried out by the method shown below.

[0026] (1) Measuring method of physical properties (A) It is based on MFR:JIS-K7210 (190 degrees C, 2.16kg load).

(B) Dense Degree: It is conformity (C) to JIS-K7112. Extrapolation dissolution end temperature by the differential scanning calorimetry (DSC) (Tem): Heat press. After carrying out weighing capacity of about 5mg sample from the fabricated 100-micrometer film, setting it in the DSC equipment made from SEIKO Electronic industry (RDC 220), carrying out a

temperature up to 170 degrees C and holding for 5 minutes at the temperature, it cools to -10 degrees C by part for 10-degree-C/in temperature fall speed. After holding for 1 minute in the state, it measured by carrying out a temperature up to the temperature of 170 degrees C by part for 10 degrees-C/of programming rates. And the DSC curve when carrying out a temperature up even to 170 degrees C from -10 degrees C was obtained. Next, based on JIS-K7121, temperature of the intersection of the line which extended the base line by the side of the elevated temperature of a DSC curve to the low temperature side, and the tangent drawn in that inclination becomes the maximum at the curve by the side of the elevated temperature of a dissolution peak was made into extrapolation melting end temperature (Tem).

[0027] (2) The physical-properties evaluation method of a laminate film (A) Bond strength: After continuing beforehand the test piece with a width of face [ of 15mm ], and a length of 90mm in the 40mm of the length directions and exfoliating a base-material layer and a lamination layer, the maximum (g/15mm) when exfoliating T type in a part for 300mm/of speeds of testing with a SHOPPA type tension tester was measured.

[0028] (B) Heat-sealing intensity : two laminate films judged in width of face of 15mm were made to pile up mutually so that a lamination layer comrade may touch, it heat sealed in the heating-plate formula heat sealer in the seal temperature of 140 degrees C, pressure 2 kgf/cm<sup>2</sup>, and time 1 second, and the maximum (g/15mm) when exfoliating the obtained sample T type in a part for 300mm/of speeds of testing with a SHIWOPPA type tension tester was measured.

[0029] (C) After having made it meet so that the lamination layer comrade of a shock-resistant on-the-strength laminate film may lap, heat sealing the three way type in the heating-plate formula heat sealer (seal width of face of 0.5mm, the seal temperature of 140 degrees C, pressure 2 kgf/cm<sup>2</sup>, time 1 second), producing the 150mmx150mm bag body and being filled up with 200 cc water into it, it remained while heat sealed similarly. And it fell so that it might be mostly in charge of parallel in a griddle with a weight [ of a size equivalent to it on the bag body ] of 1kg, and the fall height (cm) of the griddle which the seal section of a bag body destroys by one fall was measured.

[0030] [II] it blended with the corona-treatment side of an ONY base-material (nylon oriented film : emblem ONM[ by Unitika, Ltd. ] # 15 15 micrometers) layer where an example, the example examples 1-7 of comparison and the example 1 of comparison - 2 anchor-coat processing are not performed from the T die of a co-extrusion laminator by the blending ratio of coal shown in Table 1 at a base-material side -- carry out melting mixture Ethylene and 10 micrometers of alpha olefin copolymer-resin constituent layers which fabricated the pelletized resin at the resin temperature of 290 degrees C in the shape of a film It co-extrudes so that it may become 30 micrometers of high-pressure-produced-polyethylene resin (LC600made from Japanese PORIKEMU C, MFR:190-degree C 7, and density 0.919 g/cm<sup>3</sup>) layers at the opposite side, and it makes with a melting film. subsequently From the nozzle installed in the position of 30mm under the die towards the ethylene and the alpha olefin copolymer-resin side of this melting film Ozone level 12 g/m<sup>3</sup> After spraying and ozonizing air in a 1.5m<sup>3</sup>/o'clock amount, it has arranged so that the ozonization side of this ethylene and alpha olefin copolymer resin may lap with the corona-treatment side of a base-material layer, and the sticking-by-pressure lamination was carried out with an air GIAPPU 130mm sticking-by-pressure roll. Lamination speed at this time was considered as a part for 100m/. The composition of the obtained layered product is as follows. The physical properties of the laminate film (layered product) obtained 15 micrometers of nylon base-material layers, ethylene and 10 micrometers of alpha olefin copolymer-resin layers, and 30 micrometers of high-pressure-produced-polyethylene resin layers are evaluated, and the evaluation result is shown in Table 1.

[0031] Example 8 resin temperature was made into 320 degrees C, except not ozonizing, it fabricated like the example 1 and the physical properties of the obtained laminate film

(layered product) were evaluated. The evaluation result is shown in Table 1.

[0032] As the material of examples 9-15 and the example 3 of comparison - 4 base-material layers. It carried out like the example 1 except having used the polyethylene-terephthalate resin (PET : diamond foil H made from diamond HOIRUHEKISUTO, Inc. 500#12 12 micrometers), and having used ethylene and 10 micrometers of alpha olefin copolymer-resin constituent layers which fabricated the pelletized resin which was blended by the blending ratio of coal shown in Table 2 as ethylene and alpha olefin copolymer resin, and which carried out melting mixture at temperature with a resin temperature of 290 degrees C in the shape of a film. The physical properties of the obtained laminate film (layered product) are evaluated, and the evaluation result is shown in Table 2.

[0033] Example 16 resin temperature was made into 320 degrees C, except not ozonizing, it fabricated like the example 9 and the physical properties of the obtained laminate film (layered product) were evaluated. The evaluation result is shown in Table 2.

[0034] The laminate film (layered product) manufactured in the example 17 example 9 was passed the speed for 100m/in the hot blast oven heated by 100 degrees C, and heat treatment was performed for about 2 seconds. The physical properties of the obtained layered product were evaluated. The evaluation result is shown in Table 2.

0037] \*1: Ethylene butene-1 copolymer-resin material obtained according to the metallocene catalyst of MFR=35, density 0.885, and 23 % of the weight of butene-1 contents (C2-C4 copolymer).

\*2: Ethylene butene-1 copolymer-resin material obtained according to the metallocene catalyst of MFR=4, density 0.912, and 13 % of the weight of butene-1 contents (C2-C4 copolymer).

\*3: Ethylene hexene-1 copolymer-resin material obtained according to the vanadium catalyst of MFR=16, density 0.895, and 18 % of the weight of hexene -1 contents (C2-C6 copolymer).

\*4: Mitsui petrochemical company make -- the ethylene butene-1 copolymer-resin material obtained according to "A20090" MFR=18 and the vanadium catalyst of density 0.895

\*5: the product made from Japanese PORIKEMU -- "LC600A" MFR=7 and the low-density-polyethylene resin material (low density PE) of density 0.919

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(22)Date of filing : **29.10.1997** (72)Inventor : **IKEDA MUTSUOKO**

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## **(54) PRODUCTION OF LAMINATED BODY**

(57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a production method for a laminated body in which a resin film or a metallic foil and other resin layers are laminated to each other through a co-extrusion laminating method without pre-heating or post-heating the adherend in such a manner as to have a sufficient adhesive force between the layers.

**SOLUTION:** An adhesive layer (layer A) comprising (a) 1 to 85 wt.% of modified ethylene copolymer that is modified by unsaturated carboxylic acid, which contains 0.01 to 10 wt.% of carboxylic acid and whose density and MFR are 0.850 to 0.950 g/cm<sup>3</sup> and 0.05 to 50 g/10 min, respectively, (b) 1 to 59 wt.% of stickiness imparting agent and (c) 10 to 80 wt.% of a block copolymer comprising a copolymer block of a vinyl aromatic compound and a copolymer block of a conjugated diene compound or its hydro-substance and a resin layer (layer B) of a polyolefin resin or the like are laminated onto a resin film, a sheet or a metal through a co-extrusion laminating method.

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## MEANS

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[Means for Solving the Problem] That is, an ethylene system polymer denaturalizes this invention with a unsaturated carboxylic acid or its derivative, and the content of this unsaturated carboxylic acid or its derivative is 0.01 - 10 % of the weight. and the denaturation ethylene system polymer (a) which are density 0.850 - 0.950 g/cm<sup>3</sup>, and 10 0.05-50g of melt flow rates and minutes -- one to 85% of the weight Tackifier (b) At least one polymer block which consists of 1 - 59 % of the weight, and vinyl aromatic compounds, the adhesives layer (A horizon) (however, the above (a) --) which consists of a block copolymer which has at least one polymer block which consists of conjugated-diene compounds, or its hydrogenation (object c) 10-80 % of the weight (b) The total quantity of the (c) component becoming 100% of the weight And a polyolefine system resin, A polyester system resin, an ethylene-vinylacetate-copolymer saponification object, a polyamide system resin, At least one or more sorts of thermoplastics layers (B horizon) chosen from the group which consists of polycarbonate resin, a polystyrene system resin, and an acrylic resin by the co-extrusion laminating method A resin film, The manufacture method of the layered product characterized by carrying out a laminating on a sheet or a metal is offered.

[0008]

[Embodiments of the Invention] The manufacture method of the layered product which starts this invention below is explained concretely. Although the layered product obtained by the manufacture method of the layered product concerning this invention consists of (1) resin film, a sheet or a metal, (2) adhesives layers (A horizon), and (3) thermoplastics layers (B horizon) and also may turn into a multilayer layered product, it explains these each class first.

[0009] (1) With a resin film, a sheet, or a metal this invention Or one shaft or a biaxially oriented film is used. as a resin film -- a unstretched film -- specifically A polyethylene

terephthalate (PET), Copolymer PET, a polybutylene terephthalate, Polyester system resin films, such as polyethyleneterephthalate and polycyclohexylene terephthalate, Polyolefine system resin films, such as polypropylene and polyethylene, 6-nylon, 6, and 6-nylon, 6-6, 6-nylon, 12-nylon, A polyamide system resin film or K quart nylon films, such as MXD nylon, In addition, the printing film to which printing is given in various ink is used for an ethylene-vinylacetate-copolymer saponification object film, the vacuum evaporation film with which the vacuum evaporation of a silica, the aluminum, etc. has been further carried out to one side or both sides on the front face of various films, one side, or both sides. Such a resin film is usually 5-100 micrometers in thickness, and it is excellent in a mechanical strength, dampproofing, transparency, and thermal resistance while excelling in gas-proof permeability. [0010] furthermore -- as a resin sheet -- a non-extended sheet -- or one shaft or a biaxial-stretching sheet uses -- having -- concrete -- a polyethylene terephthalate (PET) Copolymer PET, a polybutylene terephthalate, polyethyleneterephthalate, Polyester system resin sheets, such as polycyclohexylene terephthalate, Polyolefine system resin sheets, such as polypropylene and polyethylene, 6-nylon, Polyamide system resin sheets, such as 6 and 6-nylon, 6-6, 6-nylon, 12-nylon, and MXD nylon, Or a K quart nylon sheet, other ethylene-vinylacetate-copolymer saponification object sheets, Furthermore, the printing sheet with which printing is given to the vacuum evaporation sheet with which the vacuum evaporation of a silica, the aluminum, etc. has been carried out to one side or both sides, one side, or both sides in various ink is used for the front face of various sheets.

[0011] Moreover, it may be tubular, for example, a metallic foil, a tabular, and the thing used copper, aluminum, iron, etc. and conventionally can be widely used for the metal used by this invention. Furthermore you may be the metal itself and kraft paper etc. may be stuck on a rear face.

[0012] (2) Adhesives layer (A horizon)

A (following a) - (c) component is included as an adhesives layer (A horizon). That is, an ethylene system polymer denaturalizes it with a unsaturated carboxylic acid or its derivative as a (a) component, and the content of this unsaturated carboxylic acid or its derivative is 0.01 - 10 % of the weight. And density 0.850 - 0.950 g/cm<sup>3</sup>, 1 - 85 % of the weight of denaturation ethylene system polymers which are 0.05-50g of melt flow rates, and 10 minutes, (b) As a component, 1 - 59 % of the weight of tackifiers, (c) It consists of resin constituents which consist of a block copolymer which has at least one polymer block which makes a principal component at least one polymer block which makes a vinyl aromatic compound a principal component as a component, and conjugated-diene compound, or 10 - 80 % of the weight of its hydrogenation object. However, the total quantity of the above (a), (b), and the (c) component is 100 % of the weight.

[0013] (i) Denaturation ethylene system polymer (a)

In this invention, the graft copolymerization of the ethylene system polymer is carried out to a denaturation ethylene system polymer (a) with a unsaturated carboxylic acid or its derivative, or this is diluted with an ethylene system polymer and denaturalized. A melt flow rate is [ the density of the suitable ethylene system polymer used for denaturation ] a copolymer with the ethylene homopolymer of 0.850 - 0.950 g/cm<sup>3</sup> or ethylene and an alpha olefin, a vinyl ester, an unsaturation carboxylate, etc. for 0.05-50g / 10 minutes. The alpha olefins which constitute an ethylene-alpha olefin copolymer are the alpha olefin which does not usually contain the cyclic molecule of carbon numbers 3-20, for example, a propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-tetrapod decene, 1-octadecene, etc., and consist of respectively independent or two or more sorts of mixture. Furthermore, an ethylene system polymer can also be used by two or more kinds, mixing. As an example, they are low-density-polyethylene (LDPE), high-density-polyethylene (HDPE), medium-density-polyethylene (MDPE), straight chain-like low-density-polyethylene (LLDPE), super-low-density-polyethylene (VLDPE), and low crystallinity ethylene-butene-1 random copolymer (EBM),

an ethylene propylene rubber, an ethylene vinylacetate copolymer, an ethylene-ethyl-acrylate copolymer, etc.

[0014] As the unsaturated carboxylic acid used for denaturation, or its derivative Unsaturated carboxylic acids, such as an acrylic acid, a maleic acid, boletic acid, a tetrahydrophthalic acid, an itaconic acid, a citraconic acid, a crotonic acid, an isocrotonic acid, and the NAJIKKU acid R (the endo-cis-bicyclo [2, 2, 1] hept-5-en -2, 3-dicarboxylic acid), or the derivative of those, for example, acid halide, an amide, imide, an anhydride, ester, etc. are mentioned, and, specifically, chlorination MARENIRU, maleimide, maleic-anhydride, anhydrous citraconic acid, and maleic-acid monomethyl, In these, an unsaturation dicarboxylic acid or its acid anhydride is suitable, and a maleic acid, the NAJIKKU acids R, or these acid anhydrides are especially suitable.

[0015] In order to manufacture a denaturation ethylene system polymer (a), well-known various methods are conventionally employable. For example, an ethylene system polymer and a unsaturated carboxylic acid or its derivative, and a radical generating agent are mixed in advance, and there is a method of making carry out melting and carrying out graft copolymerization with an extruder, or the method of dissolving an ethylene system polymer in a solvent, and adding and carrying out the graft copolymerization of a radical generating agent, a unsaturated carboxylic acid, or its derivative. In order to carry out the graft copolymerization of the aforementioned unsaturated carboxylic acid or its derivative efficiently in any case, it is desirable to react to the bottom of existence of a radical initiator. A graft reaction is usually performed at the temperature of 60-350 degrees C. The service temperature of a radical initiator is usually the range of 0.001 - 1 weight section to the ethylene system polymer 100 weight section. As a radical initiator. \*\*\*\*\* peroxide and organic per ester, for example, a benzoyl peroxide, A dichloro benzoyl peroxide, dicumyl peroxide, G t-butyl peroxide, 2, the 5-dimethyl -2, 5-JI (peroxy benzoate) hexyne - 3, 1, 4-screw (t-butylperoxy isopropyl) benzene, Lauroyl peroxide, t-butyl per acetate, 2, the 5-dimethyl -2, 5-JI (t-butylperoxy) hexyne - 3, 2, the 5-dimethyl -2, 5-JI (t-butylperoxy) hexane, t-butyl per benzoate, t-butyl per phenyl acetate, t-butyl per iso butyrate, t-butyl per-s-OKUETO, t-butyl per pivalate, and a cumyl per -- viva, there are a rate and t-butyl per diethyl acetate, other azo compounds, for example, an azobisisobutyronitril, and dimethyl azoisobutylate It is dicumyl peroxide, G t-butyl peroxide, 2, and 5-dimethyl then among these. - 2, 5-JI (t-butylperoxy) hexyne - Dialkyl peroxide, such as 3, 2, 5-dimethyl -2, 5-JI (t-butylperoxy) hexane, 1, and 4-screw (t-butylperoxy isopropyl) benzene, is desirable.

[0016] When diluting this denaturation ethylene system polymer (a) by the ethylene system polymer before the denaturation, the homotypic, or the ethylene system polymer of a different kind, the content of a unsaturated carboxylic acid or its derivative needs to be after dilution, and needs to be [ aforementioned ] within the limits.

[0017] The content of a unsaturated carboxylic acid or its derivative of such a denaturation ethylene system polymer (a) is 0.03 - 8 % of the weight especially preferably 0.02 to 9% of the weight preferably 0.01 to 10% of the weight. density -- 0.850 - 0.950 g/cm<sup>3</sup> -- desirable -- 0.852-0.948g/cm<sup>3</sup> -- especially -- desirable -- 0.855 - 0.945 g/cm<sup>3</sup> -- it is -- and a melt flow rate -- 0.05-50g / 10 minutes -- desirable -- 0.06-49g/-- they are 0.07-48g / 10 minutes especially preferably for 10 minutes

[0018] Moreover, an adhesive property is not improved for the content of a unsaturated carboxylic acid or its derivative by the thing of under the aforementioned range, but while dispersibility falls and the thing exceeding aforementioned within the limits on the other hand is inferior in the appearance of mold goods for bridge formation, an adhesive property falls. Furthermore, if density is too low, the workability at the time of a fabricating operation will get worse remarkably, and on the other hand, if too high, adhesive strength will not bear practical use low. a melt flow rate -- the above -- since it is inferior to a bond strength while it is inferior to a moldability, since it is too low, whether melt viscosity is too high in it being

out of range, it is not desirable. In addition, the melt flow rate (MFR) as used in the field of this invention is JIS. Based on K7210, the value measured on the temperature of 190 degrees C, the load of 2.16kg, and the conditions for 10 minutes is meant.

[0019] (ii) Tackifier (b)

The tackifier (b) used by this invention is a solid non-crystalline polymer in ordinary temperature, and a petroleum resin, a rosin system resin, terpene system resins, or those hydrogenation objects are desirable especially, and it can choose from a commercial thing suitably and can use. As a petroleum resin, there are an aliphatic system petroleum resin, aromatic system petroleum resins or those copolymers, these hydrogenation objects, etc., and it is specifically as commercial elegance, for example. TOHO highness resin (\*\*\*\* Petroleum resin), a pico pail (pico company), ARUKON P and M (Arakawa Chemical industry), an ad multiple independently targetable reentry vehicle (Idemitsu Petrochemical industry), a superstar tuck (RAIHI Hold), id KORETTSU (Esso Chemistry), TOHOPETORO resin (TONEN Petroleum resin), high RETTSU (Mitsui Petrochemistry), a Queen ton (Nippon Zeon Co., Ltd.), etc. are mentioned.

[0020] As a rosin system resin, natural rosin, polymerization rosin and those derivatives, for example, PENTAE list ester rosin, glycerol-ester rosin, those hydrogenation objects, etc. are mentioned, and a gum rosin, a wood rosin, rosin ester A, PERUSENA, PERUSENC (Arakawa Chemical industry), Pentalin A, Pentalin C, FORARU 105 (\*\*-ized Hercules, Inc.), etc. are specifically mentioned as commercial elegance. As a terpene system resin, there are a polyterpene system resin, terpene phenol system resins, and those hydrogenation objects, and the pico lights S and A (pico company), YS resin, chestnut ARON (Yasuhara Fats and oils), etc. are specifically mentioned as commercial elegance.

[0021] Although these tackifiers can be properly used by the use in this invention, also in these tackifiers, softening temperature (ring and ball method) is desirable, and 70-150 degrees C of 90-150-degree C things are used especially preferably. When softening temperature is too low, while it is in the inclination for a bond strength to fall, it is in the inclination for melting kneading with a hydrogenation block copolymer or an ethylene system polymer to become difficult. Moreover, in order to bring the hue of the above-mentioned constituent close to a mass color (white or transparency and colorlessness, yellow coloring prevention) as much as possible, an aliphatic system petroleum resin, aromatic system petroleum resins, or those copolymers are desirable, and especially the hydrogenation object is desirable. The rate of hydrogenation is 90% or more more preferably 80% or more.

[0022] (iii) A block copolymer or its hydrogenation object (c)

The block copolymer used by this invention or its hydrogenation object (c) is a hydrogenation block copolymer which comes to carry out hydrogenation of the block copolymer of a vinyl aromatic compound and a conjugated-diene compound preferably. When it presupposes that block copolymers are the polymer block with which Block A consists of a vinyl aromatic compound, and a polymer block with which Block B consists of a conjugated-diene compound, As a making [ into a principal component ]-vinyl aromatic compound which constitutes the polymer block section A from block copolymer expressed with general formula A-B, A-B-A, B-A-B-A, A-B-A-B-A, etc. compound, one or more sorts are chosen from from, for example among styrene, an alpha methyl styrene, vinyltoluene, etc., and styrene is desirable especially.

[0023] Moreover, as a conjugated-diene compound which constitutes the polymer block B, one or more sorts are chosen from from, for example among butadiene, isoprene, 1, and 3-pentadienes etc., and a butadiene, isoprenes, and such combination are desirable especially. The content of the polymer block which consists of a vinyl aromatic compound used as Block A is 10 - 70 % of the weight preferably ten to 80% of the weight. At least, even if there are many contents of this polymer block, its bond strength falls and is not more desirable than the above-mentioned range.

[0024] Generally, its thermal stability especially improves and it is preferably desirable [ the rate of hydrogenation of the polymer block which consists of a conjugated-diene compound / it is 95% or more especially preferably, and ] so that it is high 90% or more more preferably 80% or more 50% or more.

[0025] The number average molecular weight of a block copolymer or its hydrogenation object (c) is 20,000-300,000 still more preferably 10,000 to about 400,000 preferably. Even if molecular weight is too large and it is too small, when a bond strength serves as a fall inclination and its number average molecular weight is too large, it has the inclination for the processability of this constituent to fall.

[0026] Moreover, even if the number average molecular weight of this block copolymer or its hydrogenation object (c) is 400,000 or less, when higher, When a process oil, liquid polybutadiene, and number average molecular weight add 1 - 40 weight section grade for the fluid improvement agent chosen from 6,000 or less olefin system waxes etc. to a block copolymer or its hydrogenation (object c) 100 weight section, it becomes possible to suppress the fall of a bond strength and processability, and is an effective means. The block copolymer which has A-B-A structure is desirable, and it is commercial elegance concretely. There are a "Cali FREX" TR type (shell chemistry company make) and a vector (product made from DEKISHIKO) as a styrene-butadiene system hydrogenation type block copolymer as "SEPUTON" 2000 type (Kuraray Make), a styrene-butadiene system block copolymer, and a styrene-isoprene system block copolymer as a "tough tech" H type (Asahi Chemical Industry Co., Ltd. make), "Clayton" G1600 type (product made from shell chemistry), and a styrene-isoprene system hydrogenation type block copolymer. Moreover, styrene-isoprene system hydrogenation type block-copolymer "SEPUTON" 1000 type (Kuraray Make) which has A-B structure, "Clayton" G1700 type (shell chemistry company make), etc. are mentioned.

[0027] Furthermore, the above-mentioned block copolymer can also be used by two or more kinds, mixing.

[0028] (3) How to obtain the constituent of \*\*\*\*\* of the constituent for an adhesives layer (A horizon) What is necessary is just to adopt a granulation or the method of pulverizing after melting kneading by the 1 shaft extruder, the twin screw extruder, the kneader, the Banbury mixer, etc. after the method of mixing variously the aforementioned denaturation ethylene system polymer (a), a tackifier (b) and a block copolymer, or its hydrogenation object (c) with a well-known method, for example, a Henschel mixer, V-blender, a ribbon blender, a tumbler blender, etc., or mixture. the loadings of each above-mentioned component -- aforementioned denaturation ethylene system (polymer a) 1-85 % of the weight -- desirable -- 2 - 83 % of the weight -- further -- desirable -- 3 - 80 % of the weight, and (Tackifier b) 1-59 % of the weight -- desirable -- 2 - 55 % of the weight -- further -- desirable -- 3 - 50 % of the weight -- and -- \*\* -- a block copolymer or its hydrogenation object (c) -- it is 10 - 75 % of the weight still more preferably ten to 78% of the weight preferably ten to 80% of the weight Since a denaturation ethylene system polymer (a) is in the inclination for adhesive strength to decline also in 85-% of the weight super-\*\*, at least less than 1% of the weight and the adhesive strength to each adherend declines [ a tackifier (b) ] at less than 1 % of the weight. Preferably, when it, on the other hand, exceeds 59 % of the weight, a fluidity becomes high too much and it is in the inclination for a moldability to get worse, and from 10 % of the weight, even if there are more block copolymers or its hydrogenation objects (c) than at least 80 % of the weight, they are in the inclination for an adhesive property to fall.

[0029] Moreover, in addition to the aforementioned component, into this constituent, you may blend a heat-resistant stabilizer, a weathering stabilizer, an antistatic agent, a pigment, a color, a rusting inhibitor, etc. if needed.

[0030] (4) Thermoplastics layer (B horizon)

In this invention, the resin chosen from a polyolefine system resin, a polyester system resin, an ethylene-vinylacetate-copolymer saponification object, a polyamide system resin,

polycarbonate resin, a polystyrene system resin, and an acrylic resin is used as a thermoplastics layer (B horizon).

[0031] The polyolefine system resin used for a thermoplastics layer (B horizon) is independent or the crystalline polymer which makes these the principal component of the ethylene which is the alpha olefin of carbon numbers 2-4, a propylene, and 1-butene. Although polyethylene, polypropylene, and a poly 1 butene are specifically mentioned as these polyolefines As long as not only a homopolymer but these olefins are made into a principal component, the graft copolymer by which graft denaturation was carried out also including the copolymer with vinyl compounds, such as the alpha olefin of other carbon numbers 2-20 or vinyl acetate, a vinyl chloride, an acrylic acid, a methacrylic acid, and styrene, with unsaturated carboxylic acids, such as a maleic anhydride, a maleic acid, and an acrylic acid, or the derivative of those is sufficient as each of these. Furthermore, these polyolefines may be mixture. As an example of the aforementioned polyethylene, a high-pressure-process low density polyethylene (LDPE), an ethylene propylene rubber, an ethylene-1-butene copolymer, an ethylene-4-methyl-1-pentene polymer, an ethylene-1-hexene copolymer, a high density polyethylene (HDPE), an ethylene vinylacetate copolymer, an ethylene-acrylic-acid copolymer, an ethylene-acrylic-ester copolymer, etc. are mentioned, for example. In these, since LDPE, an ethylene-alpha olefin random copolymer, an ethylene vinylacetate copolymer, etc. are excellent in transparency and low-temperature heat-sealing nature, it is desirable, and the thing of the range 0.910 - 0.960 g/cm<sup>3</sup> and whose melting point density is especially 100-135 degrees C is desirable. In addition, although especially limitation is not carried out, the thing of the range for 0.01-30g / 10 further 0.1-10g / per minute, and 10 minutes is usually desirable [ the melt flow rate of polyethylene ] from the point of a moldability.

[0032] As an example of the aforementioned polypropylene, propylene random copolymers (a propylene content is usually 95% or more preferably 90% or more), such as a polypropylene (propylene homopolymer) and propylene-ethylene random copolymer, a propylene-ethylene-1-butene random copolymer, and a propylene-1-butene random copolymer, a propylene-ethylene block copolymer (an ethylene content is usually 5-30-mol %), etc. are mentioned, for example. In these, since a homopolymer and a random copolymer are excellent in transparency, it is desirable, and since the random copolymer especially whose melting point is 130-140 degrees C is excellent in heat-sealing nature, it is desirable. In addition, although especially limitation is not carried out, the thing of the range for further 0.5-10g / 10 minutes is usually desirable [ the melt flow rate of a propylene ] from the point of a moldability for 0.5-30g / 10 minutes.

[0033] As an example of the aforementioned poly 1 butene, 1-butene homopolymer, a 1-butene-ethylene copolymer, a 1-butene-propylene copolymer, and a 1-butene-4-methyl-1-pentene copolymer are mentioned, for example. In addition, although especially the melt flow rate of a poly 1 butene is not limited, the thing of the range for 0.01-100g / 10 further 0.03-30g / per minute, and 10 minutes is usually desirable from the point of a moldability.

[0034] About the polyester used for a thermoplastics layer (B horizon) A terephthalic acid, an isophthalic acid, a diphenyl ether -4, 4-dicarboxylic acid, Aromatic dicarboxylic acids, such as naphthalene -1, 4- or 2, and 6-dicarboxylic acid, The acid component of dicarboxylic acids, such as alicycle group dicarboxylic acids, such as aliphatic dicarboxylic acids, such as oxalic acid, a succinic acid, an adipic acid, a sebacic acid, and an undeca dicarboxylic acid, and a hexahydro tele FUTERU acid Ethylene glycol, a propylene glycol, 1, 4-butanediol, Alicycle group glycols, such as alicycle group glycols, such as neopentyl glycol, and cyclohexane dimethanol, It is what consists of glycol components, such as aromatic dihydroxy compounds, such as bisphenol A. A polyethylene terephthalate (PET), Copolymer PET, a polybutylene terephthalate, polyethylenenaphthalate, poly cyclo hexyne terephthalate, etc. are mentioned. It is thermoplastic polyester resin more than whose 80 mol % of a glycol component especially a desirable thing is a polyethylene terephthalate (PET) in this, more than 80 mol % of a



dicarboxylic-acid component is usually a terephthalic acid, and is ethylene glycol.

Furthermore, Copolymer PET may also be the mixture of PET and other polyester.

[0035] As an ethylene-vinylacetate-copolymer saponification object used for a thermoplastics layer (B horizon), an ethylene content is desirable and 15-60-mol % and the thing to which the degree of saponification saponified the 25-50-mol % of ethylene vinylacetate copolymer still more preferably so that it might become 90% or more preferably 50% or more are used. Since it is easy to pyrolyze, and melting fabrication is difficult, and is inferior also to ductility and water resistance is [ that it absorbs water and is easy to swell ] inferior when there are too few ethylene contents, it is not desirable. On the other hand, when there are too many ethylene contents, there is an inclination for gas-proof permeability to fall. Moreover, when the degree of saponification is too low, there is an inclination for gas-proof permeability to fall.

[0036] As a polyamide system resin used for a thermoplastics layer (B horizon), a hexamethylenediamine, A deca methylene diamine, a dodeca methylene diamine, 2 and 2, 4- or 2 and 4, a 4-trimethyl hexamethylenediamine, 1 and 3- or 1, 4-screw (aminomethyl) cyclohexane, a screw (p-amino cyclohexyl methane), Aliphatic series, such as aliphatic series, such as m- or p-xylylene diamine, an alicycle group, which aromatic diamine and aromatic adipic acid, a suberic acid, a sebacic acid, a cyclohexane dicarboxylic acid, a terephthalic acid, and an isophthalic acid, an alicycle group, and a polycondensation with which aromatic dicarboxylic acid. The mixture of the copolymerization polyamide which consists of polyamides obtained from lactams, such as a polyamide obtained according to condensation of amino carboxylic acids, such as a polyamide obtained, an epsilon aminocaproic acid, and a 11-amino undecane carboxylic acid, an epsilon caprolactam, and omega-RAURO lactam, or these components etc. is illustrated. Specifically, nylon 6, Nylon 66, Nylon 610, nylon 9, Nylon 11, Nylon 12, nylon 6 / 66, Nylon 66 / 610, nylon 6/11, etc. is mentioned. In these, the nylon 6 and Nylon 66 in which the melting point, rigidity, etc. are excellent are desirable. Moreover, although especially limitation is not carried out, and 0.5 or more polyamides are usually used for relative viscosity  $\eta_{sp}/c$  (it measures in a JIS K6810 or 98% sulfuric acid), 2.0 or more things of molecular weight are desirable especially.

[0037] The polycarbonate resin used for a thermoplastics layer (B horizon) is various polycarbonates which a dihydroxy compound, a phosgene, or diphenyl carbonate is made to react by the well-known method, and are obtained. As a dihydroxy compound, they are - dihydroxy diphenylmethane, and - dihydroxydiphenyl-n-butane, and - dihydroxy diphenylmethane, and hydroquinone, resorcinol, 4, and 4 '4, 4'-dihydroxy bibenzyl, 4, and 4 '4, 4'-dihydroxydiphenyl heptane, 4, and 4 '4, 4'-dihydroxydiphenyl -2 and 2-propane (bisphenol A). 4, 4'-dihydroxy -3, 3'-dimethyl diphenyl -2, 2-propane, 4, 4'-dihydroxy -3, 3'-diphenyl diphenyl -2, 2-propane, - dihydroxy dichloro diphenyl -2, 2-propane, and 4 and 4 '4, 4'-dihydroxydiphenyl -1, 1-cyclopentane, - dihydroxydiphenyl -1, 1-cyclohexane, and 4 and 4 '4, 4'-dihydroxydiphenyl methylphenyl methane, - dihydroxydiphenyl ethyl phenylmethane, and 4 and 4 '4, 4'-dihydroxydiphenyl - 2, 2, and 2-TORIKURORO -1, 1-ethane, 2 and 2'-dihydroxydiphenyl, 2, 6-dihydroxy naphthalene, - dihydroxy diphenyl-ether, and 4 and 4 '4, 4'-dihydroxy -3, - dichlorodiphenyl ether, and 3 '4, 4'-dihydroxy -2, 5-diethoxy phenyl ether, etc. are used. Among these, since the polycarbonate using 4 and 4'-dihydroxydiphenyl -2 and 2-propane (bisphenol A) is excellent in a mechanical performance and transparency, it is desirable.

[0038] The polystyrene system resin used for a thermoplastics layer (B horizon) is a resin which made the subject the styrene of copolymers, such as a homopolymer of styrene, styrene and acrylonitrile, and methyl (meta) acrylate, or those rubber denaturation objects, and the thermoplastics specifically called polystyrene, the high impact polystyrene (rubber combination polystyrene), the AS resin (SAN), ABS, etc. is used. polystyrene -- usually -- a melt flow rate -- 0.1-50g/-- it is the thing of the range for 1-20g / 10 minutes preferably for 10 minutes The thing besides the above-mentioned range tends to be inferior to a moldability in



MFR anyway.

[0039] A polymethylacrylate, polyacrylic-acid ethyl, polyacrylic-acid butyl, polyacrylic-acid-2-ethylhexyl, a polymethyl methacrylate, a polyacrylonitrile, the poly methacrylonitrile, a methyl-methacrylate-acrylonitrile copolymer, a methyl-methacrylate-alpha-methyl-styrene copolymer, etc. can be illustrated as the acrylic resin used for a thermoplastics layer (B horizon). Furthermore, you may be a styrene acrylonitrile copolymer, a styrene-acrylonitrile-butadiene copolymer, a styrene-methyl-methacrylate copolymer, etc. A polyacrylonitrile and styrene-acrylonitrile-butadiene copolymer is desirable especially. These acrylic resins are the ranges which can choose suitably from commercial elegance, and can use, and do not spoil the effect of this invention, and may blend additives, such as various plasticizers, a stabilizer, an inorganic filler, an antistatic agent, and a pigment.

[0040] (5) The constituent which constitutes an adhesives layer (A horizon) from a manufacture method this invention of a layered product, The resin which constitutes at least one or more kinds of thermoplastics layers (B horizon) is fused with a respectively separate extruder. The dice of the structure of after [ melting ] two-layer or three layers or more is supplied separately. this (1) resin film, A layered product can be manufactured, when they carry out a co-extrusion lamination on a sheet or a metal, as (2) adhesives layers (A horizon) touch the aforementioned (1) resin film, a sheet, or a metal. The die used here is the so-called flat die, and any of the single-manifold form which used the black box, or multi--manifold form may be used for it. Moreover, you may manufacture a layered product by performing the sand lamination which extrudes a glue line (A horizon) among the base materials which are a resin film, a sheet, or a metal. this time -- a resin film, a sheet, or a metal -- not necessarily -- preheating -- or it is not necessary to carry out afterbaking

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## EXAMPLE

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[Example] Although an example and the example of comparison explain this invention below, this invention is not limited to these examples.

[0042] an example 1. ethylene-butene copolymer (density: -- 0.920 g/cm<sup>3</sup> and MFR190 degree-C-2.16 kg : 2g/-- for 10 minutes) melting point: -- a 45-% of the weight and 124-degree-C maleic-anhydride denaturation ethylene-butene copolymer (maleic-anhydride content: -- 1% of the weight) 121-degree C 15 % of the weight, 2.16 kg : MFR190 degree-C-1g /, 10 minutes, density:0.919 g/cm<sup>3</sup>, the melting point : 25 % of the weight (an aromatic system hydrogenation type petroleum resin, number-average-molecular-weight:710, specific gravity:0.998, softening temperature:115 degree C) of tackifiers, a styrene-butadiene copolymer hydrogenation object (styrene content: -- 20% of the weight) It mixes for 5 minutes with a 50l. V type blender in advance by the blending ratio of coal (6 kg : MFR200 degree-C-9.5g /, 10 minutes, and density:0.98g/cm<sup>3</sup> 15 % of the weight), and is about a twin screw extruder PCM 30 (30mmphi, ratio-of-length-to-diameter=32, Ikegai Corp. make). The constituent which is used, carries out melting kneading with the temperature of 180 degrees C, screw-speed 100rpm, and the extrusion outlet of 5kg, extrudes in the shape of a string, cuts after cooling, and is used for an adhesives layer was obtained.

[0043] This constituent was used as the adhesives layer (A horizon). Moreover, as a resin layer (B horizon), they are a low density polyethylene (tradename LM38 Mitsubishi Chemical make) or polypropylene (as tradename floor line25R (Mitsubishi Chemical make) and a gas barrier nature resin). a polyester system resin (tradename PET-G 6763, specific gravity:1.27, and intrinsic-viscosity: -- 0.75 dl/g) the Eastman Kodak Co. make and an ethylene-vinylacetate-copolymer saponification object (tradename Eval EP-G156 and ethylene

Concentration: 70% / Density: 1.12 g/cm<sup>3</sup>, melting point: 224 degrees C, Kuraray Make, a polyamide system resin (tradename nova tech 1020CA2 and melting point: -224 degrees C) The Mitsubishi Chemical make, a polycarbonate (tradename you pyrone E2000, specific gravity:1.2, Mitsubishi Gas Chemical Co., Inc. make), A polystyrene system resin (tradename DENKA styrol HI-E -4, specific gravity:1.04, melt index:3.5, DENKI KAGAKU KOGYO K.K. make), An acrylic resin: The polyacrylonitrile (tradename BAREKKUSU 3000N, specific gravity:1.15, melt index:3, Mitsui Toatsu Chemicals, Inc. make) was used.

[0044] The following biaxially oriented films or aluminum foil were used for the resin film, sheet, or metal which constitutes a layered product in this example.

O-PET (extension polyethylene terephthalate) #12 (12-micrometer \*\*)

O-Ny (extension nylon) #15 (15-micrometer \*\*)

O-PP (extension polypropylene) #20 (20-micrometer \*\*)

O-EVOH (extension ethylene-vinylacetate-copolymer saponification object) #12 (12-micrometer \*\*)

aluminum foil #7 (it is adhesion rear-face reinforcement 30-micrometer \*\* at PET) (7-micrometer \*\*)

SiOx vacuum evaporation O-PET # (it is silica vacuum evaporation extension polyethylene terephthalate to adhesion side) 12 (12-micrometer \*\*)

K-Ny (extension nylon made into the adhesion side K quart) #15 (15-micrometer \*\*)

Printing film (film which gave poor printing on O-PP) #20 (20-micrometer \*\*)

[0045] By the two-sort two-layer co-extrusion T die film fabricating method, the bed depth was set to 10 micrometers / 30 micrometers in the adhesives layer (30mmphi) / resin layer (65mmphi) from the resin film, sheet, or metal side as lamination, and the layered product was manufactured with the following molding temperature.

[0046] Polyester system resin = 275 degree-C polyamide system resin = 250 degree-C ethylene-vinylacetate-copolymer saponification object = 230 degree-C acrylic resin = 220 degree-C styrene-resin = 220 degree-C polycarbonate resin = 275 degree-C polyolefine system resin = 230-degree-C fabrication speed was set as a part for 60m/.

[0047] It is JIS about the layer indirect arrival force (g/10mm) of a resin film, a sheet or a metal, and a thermoplastics layer (B horizon). Based on K-6854, it measured on condition that the following.

Ablation width of face: 10mm desquamative state: T Peel ablation ablation temperature: It is measurement ambient temperature by 50mm/. : 23 degrees C. [0048] For a certain reason, what furthermore needs voile evaluation depending on a use was performed by the following method.

Voile processing (1)

The layered product (aluminum foil was used) obtained in the above-mentioned manufacturing method was heat sealed to the saccate, the following contents were cooled in 23 degrees C after processing for 30 minutes in 100-degree C steam after 100 cc restoration (3 hours), and the sample was obtained.

[0049] contents water: -- vinegar: -- mixture of cooking oil = 1:1:1 [0050] Voile processing (2)

The layered product (resin multilayer film) obtained in the above-mentioned manufacturing method was heat sealed to the saccate, water was made into contents, after 100 cc restoration, it cooled at 23 degrees C after processing for 30 minutes in the 80-degree C thermostat (3 hours), and the sample was obtained.

[0051] The procedure same also about the following examples and examples of comparison as an example 1 performed. It indicates, only by being attached to the manufacture method of the constituent used for an adhesives layer (A horizon), and the evaluation result is shown in Table 1 and 2.

[0052] an example 2. low density polyethylene (density: -- 0.919 g/cm<sup>3</sup> and MFR190 degree-

C-2.16 kg : 14g/-- for 10 minutes) melting point: -- a 30-% of the weight and 106-degree-C maleic-anhydride denaturation ethylene-butene copolymer (maleic-anhydride content: -- 1% of the weight) 2.16 kg : MFR190 degree-C-1g /, 10 minutes, the melting point : 121 degrees C, density 0.919 g/cm<sup>3</sup> 15 % of the weight, 25 % of the weight (an aromatic system hydrogenation type petroleum resin, number-average-molecular-weight:860, softening temperature:140 degree C) of tackifiers, a styrene-butadiene copolymer hydrogenation object (styrene content: -- 30% of the weight) It mixes for 5 minutes with a 50l. V type blender in advance 98% for 5 kg : MFR200 degree-C-3.5g /, and 10 minutes by the with a rate [ of hydrogenation ] 30-% of the weight blending ratio of coal, and is about a twin screw extruder PCM 30 (30mmphi, ratio-of-length-to-diameter=32, Ikegai Corp. make). It used, melting kneading was carried out with the temperature of 180 degrees C, screw-speed 100rpm, and the extrusion outlet of 5kg, and it extruded in the shape of a string, and cut after cooling, and the constituent was obtained.

[0053] an example 3. maleic-anhydride denaturation hydrogenation ethylene-butene copolymer (maleic-anhydride content: -- 1% of the weight) Density 0.880 g/cm<sup>3</sup>, 10 2.16 kg : MFR190 degree-C-1g /, minutes, melting point: -- 72-degree-C 50 % of the weight and a tackifier (an aromatic system hydrogenation type petroleum resin --) molecular weight 710, specific gravity 0.998, 30 % of the weight of softening temperatures of 115 degrees C, and a styrene-butadiene copolymer hydrogenation object (styrene content: -- 13% of the weight) It mixes for 5 minutes with a 50l. V type blender in advance 98% for 5 kg : MFR200 degree-C-8g /, and 10 minutes by the with a rate [ of hydrogenation ] 20-% of the weight blending ratio of coal, and is about a twin screw extruder PCM 30 (30mmphi, ratio-of-length-to-diameter=32, Ikegai Corp. make). It used, melting kneading was carried out with the temperature of 180 degrees C, screw-speed 100rpm, and the extrusion outlet of 5kg, and it extruded in the shape of a string, and cut after cooling, and the constituent was obtained.

[0054] an example 4. maleic-anhydride denaturation ethylene-butene copolymer (maleic-anhydride content: -- 0.4% of the weight) Density 0.880 g/cm<sup>3</sup>, 10 2.16 kg : MFR190 degree-C-4g /, minutes, melting point: -- 72-degree-C 80 % of the weight and a tackifier (a beta-pinene-terpene system resin --) number average molecular weight 820, 10 % of the weight of softening temperatures of 112 degrees C, and a styrene-butadiene copolymer hydrogenation object (styrene content: -- 29% of the weight) It mixes for 5 minutes with a 50l. V type blender in advance 98% for 5 kg : MFR200 degree-C-10g /, and 10 minutes by the with a rate [ of hydrogenation ] 10-% of the weight blending ratio of coal, and is about a twin screw extruder PCM 30 (30mmphi, ratio-of-length-to-diameter=32, Ikegai Corp. make). It used, melting kneading was carried out with the temperature of 180 degrees C, screw-speed 100rpm, and the extrusion outlet of 5kg, and it extruded in the shape of a string, and cut after cooling, and the constituent was obtained.

[0055] Example of comparison 1. low density polyethylene (density 0.919 g/cm<sup>3</sup>, and ten 2.16 kg : MFR190 degree-C-14g /, and parts) 45 % of the weight of 106-degree C melting points, and an ethylene propylene rubber (C3 content: -- 27% of the weight) 20-degree C 15 % of the weight, 2.16 kg : MFR190 degree-C-0.7g /, 10 minutes, the melting point : a maleic-anhydride denaturation ethylene-butene copolymer (maleic-anhydride content: -- 1% of the weight) It mixes for 5 minutes with a 50l. V type blender in advance for 2.16 kg : MFR190 degree-C-1g /, and 10 minutes by density:0.919 g/cm<sup>3</sup> and the 121-degree-C melting point [ 40 % of the weight ] blending ratio of coal, and is about a twin screw extruder PCM 30 (30mmphi, ratio-of-length-to-diameter=32, Ikegai Corp. make). It used, melting kneading was carried out with the temperature of 180 degrees C, screw-speed 100rpm, and the extrusion outlet of 5kg, and it extruded in the shape of a string, and cut after cooling, and the constituent was obtained.

[0056] Example of comparison 2. low density polyethylene (density 0.919 g/cm<sup>3</sup>, and ten 2.16 kg : MFR190 degree-C-14g /, and parts) 45 % of the weight of 106-degree C melting

points, and an ethylene propylene rubber (C3 content: -- 27%) 20-degree C 15 % of the weight, 2.16 kg : MFR190 degree-C-0.7g /, 10 minutes, the melting point : a maleic-anhydride denaturation ethylene-butene copolymer (maleic-anhydride content: -- 1% of the weight) It mixes for 5 minutes with a 50l. V type blender in advance for 2.16 kg : MFR190 degree-C-1g /, and 10 minutes by density:0.919 g/cm<sup>3</sup> and the 121-degree-C melting point [ 40 % of the weight ] blending ratio of coal, and is about a twin screw extruder PCM 30 (30mmphi, ratio-of-length-to-diameter=32, Ikegai Corp. make). It used, melting kneading was carried out with the temperature of 180 degrees C, screw-speed 100rpm, and the extrusion outlet of 5kg, and it extruded in the shape of a string, and cut after cooling, and the constituent was obtained. The resin constituent furthermore obtained above was mixed 50% of the weight, 50 % of the weight (V208M) of EVAs was mixed for 5 minutes with the 50l. V type blender, and the obtained sample was similarly estimated as the example 1.

[0057] Example of comparison 3. low density polyethylene (density 0.919 g/cm<sup>3</sup>, and ten 2.16 kg : MFR190 degree-C-14g /, and parts) 45 % of the weight of 106-degree C melting points, and an ethylene propylene rubber (C3 content: -- 27%) 20-degree C 15 % of the weight, 2.16 kg : MFR190 degree-C-0.7g /, 10 minutes, the melting point : a maleic-anhydride denaturation ethylene-butene copolymer (maleic-anhydride content: -- 1% of the weight) It mixes for 5 minutes with a 50l. V type blender in advance for 2.16 kg : MFR190 degree-C-1g /, and 10 minutes by density:0.919 g/cm<sup>3</sup> and the 121-degree-C melting point [ 40 % of the weight ] blending ratio of coal, and is about a twin screw extruder PCM 30 (30mmphi, ratio-of-length-to-diameter=32, Ikegai Corp. make). It used, melting kneading was carried out with the temperature of 180 degrees C, screw-speed 100rpm, and the extrusion outlet of 5kg, and it extruded in the shape of a string, and cut after cooling, and the constituent was obtained. The resin constituent furthermore obtained above was mixed 50% of the weight, 50 % of the weight (Nippon Oil RB4200) of EMA was mixed for 5 minutes with the 50l. V type blender, and the obtained sample was similarly estimated as the example 1.

[0058] an example of comparison 4. ethylene-butene copolymer (density: -- 0.88 g/cm<sup>3</sup> and MFR190 degree-C-2.16 kg : 1g/-- for 10 minutes) melting point: -- a 50-% of the weight and 72-degree-C maleic-anhydride denaturation ethylene-butene copolymer (maleic-anhydride content: -- 1% of the weight) 2.16 kg : MFR190 degree-C-1g /, 10 minutes, density:0.919 g/cm<sup>3</sup>, 20 % of the weight of 121-degree-C melting points, It mixes for 5 minutes with a 50l. V type blender in advance by the blending ratio of coal of 30 % of the weight of tackifiers (an aromatic system hydrogenation type petroleum resin, number-average-molecular-weight:860, specific gravity:0.999, softening temperature:140 degree C), and is about a twin screw extruder PCM 30 (30mmphi, ratio-of-length-to-diameter=32, Ikegai Corp. make). It used, melting kneading was carried out with the temperature of 180 degrees C, screw-speed 100rpm, and the extrusion outlet of 5kg, and it extruded in the shape of a string, and cut after cooling, and the constituent was obtained.

[0059]